

VISIT...

LANZAROTE
Caliente.COM

CALCIUM

[7440-70-2]

Symbol: Ca; atomic number 20; atomic weight 40.078; a Group IIA (Group 2) alkaline-earth metallic element; ionic radius 1.06 Å (Ca²⁺); electron configuration [Ar]4s²; valence state +2; standard electrode potential, $E^\circ = -2.87\text{V}$; stable isotopes and their abundance: Ca-40 (97.00%), Ca-44 (2.06%); Ca-42 (0.64%), Ca-48 (0.18%), Ca-43 (0.145%), and Ca-46 (0.003%); also the element has six unstable isotopes of which Ca-41 has the longest half-life, 1.1×10^5 yr (decay mode: electron capture), and Ca-38 has shortest half life 0.66 sec (β -decay).

Occurrence and Uses

A few calcium compounds, such as calcium oxide and calcium carbonate have been known since ancient times. The metal was isolated by Davy in 1808. Earlier its amalgam was prepared by Berzelius and Pontin. Calcium is the fifth most abundant element in the earth's crust, constituting 4.15 % by weight. Its concentration in sea water is 412 mg/L. Calcium is a highly reactive metal and is never found in free elemental form. Its compounds, however, are widely distributed in nature. Some of its common ores are limestone (CaCO₃), gypsum (CaSO₄·2H₂O), fluorite (CaF₂), anorthite (CaAl₂Si₂O₈) and apatite (Ca₅FP₃O₁₂). It also occurs in living matter, as an essential element in bones, teeth, shell, corals, and plant leaves. It constitutes about 2% of body weight, found mostly in bones and teeth. Its concentration in the blood is about 100 mg/L, found in blood proteins and serum.

The few limited applications of calcium are mostly in metallurgy. It is used to produce alloys with aluminum, lead, beryllium, copper, silicon, and other metals; as a desulfurizer, decarburizer, and deoxidizer for ferrous and non-ferrous alloys; for removal of bismuth from lead; and as a reducing agent for zirconium, uranium, thorium, and other metals. Minor, non-metallurgical applications include dehydration of organic solvents; purification of helium, argon, and other inert gases to remove nitrogen and other impurities; and as a "getter" for residual gases in vacuum tubes. Calcium compounds have numerous applications (see individual compounds).

Physical Properties

Bright, silvery-white metal; face-centered cubic crystal structure ($\alpha = 0.5582$ nm) at ordinary temperatures, transforming to body-centered cubic form ($\alpha = 0.4407$) at 430°C; density 1.54 g/cm³ at 20°C; hardness 2 Mohs, 17 Brinell (500 kg load); melts at 851°C; vaporizes at 1,482°C; electrical resistivity 3.43 and 4.60 microhm-cm at 0° and 20°C, respectively; modulus of elasticity 3–4×10⁶ psi; mass magnetic susceptibility +1.10×10⁻⁶ cgs; surface tension 255 dynes/cm; brick-red color when introduced to flame (flame test); standard reduction potential $E^\circ = -2.87\text{V}$

Manufacture

Calcium may be obtained by electrolytic or thermal reduction of its salts.

Electrolytic reduction involves electrolysis of partially molten calcium chloride at 780° to 800°C in a graphite lined steel vessel. The method requires precise control of temperature and current. The solid deposit of metal produced may contain entrapped salt and impurities such as chlorine and nitrogen. It is re-melted to reduce impurity levels.

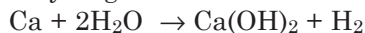
Currently, thermal reduction processes have replaced the electrolysis method. The starting material in these methods is limestone, which is calcined to produce calcium oxide. The latter is ground, mixed and compacted with aluminum, and reduced at temperatures between 1,000° to 1,200°C under vacuum. Calcium vapors formed in low yield under such thermodynamic conditions are transferred from the reactor and condensed in cool zones, thus shifting the equilibrium to allow formation of more calcium vapors. The reactions are as follows:



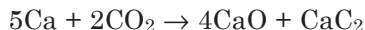
Reactions

Calcium forms divalent compounds. At ordinary temperatures it does not oxidize readily in dry air. However, at 300°C the reaction is rapid in dry oxygen. The oxidation can occur at ambient temperatures in moist air. Reaction with hydrogen at 400°C gives calcium hydride, CaH_2 . Ca metal reacts with a number of nonmetallic elements forming their corresponding binary compounds. While the reaction with fluorine occurs at ambient temperatures, other elements combine only at elevated temperatures in the range 300–900°C. Calcium combines with chlorine, bromine and iodine at 400°C and nitrogen at 900°C forming calcium halides or nitride. With sulfur, phosphorus, carbon and boron, the products are the sulfide CaS , phosphide Ca_3P_2 , carbide CaC_2 , and boride Ca_3B_2 , respectively.

Calcium reacts vigorously with water at ordinary temperatures with the evolution of hydrogen:

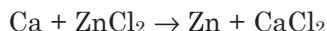


Violent reactions occur in dilute mineral acids with evolution of hydrogen. Ca reacts with carbon dioxide on heating, forming calcium oxide and calcium carbide:



Calcium combines with a number of metals at elevated temperatures forming alloys and intermetallic compounds.

Calcium is a strong reducing agent and can reduce most metal oxides and halides into their metals at elevated temperatures. It can reduce all the lower electropositive metals; e.g.



Analysis

Calcium may be analyzed by several instrumental techniques such as atomic absorption and emission spectrophotometry, ICP-MS, neutron activation, and x-ray fluorescence and diffraction methods. For all these techniques,

except the x-ray methods, the compounds of calcium must be digested in aqueous medium and diluted sufficiently prior to analysis. The metal may be measured at the wavelength 422.7nm by flame-AA or 317.93 or 315.89nm by ICP-AES. Soluble calcium compounds in water also may be measured by EDTA complexometric titration using Eriochrome Black or Calmagite indicator. Magnesium interferes with this test.

Hazard

Calcium is nontoxic. It can be handled safely. However, contact with acids, oxidizing agents or oxidizable substances can progress to explosive reactions.

CALCIUM CARBONATE

[471–34–1]

Formula: CaCO_3 ; MW 100.09

Occurrence and Uses

Calcium carbonate occurs in nature as limestone in various forms, such as marble, chalk, and coral. It is probably the most widely-used raw material in the chemical industry. It has numerous applications, primarily to produce cement, mortars, plasters, refractories, and glass as building materials. It also is used to produce quicklime, hydrated lime and a number of calcium compounds. It is produced either as powdered or precipitated calcium carbonate. The latter consists of finer particles of greater purity and more uniform size. They also have many important commercial applications. Various grades of precipitated calcium carbonate are used in several products, such as textiles, papers, paints, plastics, adhesives, sealants, and cosmetics.

Physical Properties

Calcium carbonate occurs in two forms—hexagonal crystal known as calcite, and orthorhombic form, aragonite. Calcite decomposes on heating at 825°C, aragonite melts at 1,339°C (at 102.5 atm). Density 2.71 g/cm³ (calcite), 2.83 g/cm³ (aragonite); insoluble in water (15mg/L at 25°C); K_{sp} 4.8×10^{-9} ; soluble in dilute mineral acids.

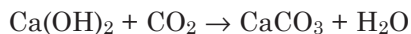
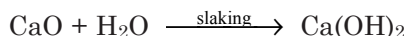
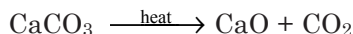
Thermochemical Properties

ΔH_f°	–288.6 kcal/mol
ΔG_f°	–269.9 kcal/mol
S°	21.92 cal/degree mol
C_p	19.9 cal/degree mol

Production

Calcium carbonate is obtained from natural limestone deposits. The purified compound, known as precipitated calcium carbonate, is synthesized from limestone. Limestone is calcined to calcium oxide and carbon dioxide in a kiln. The products are recombined after purification. Calcium oxide is hydrated

with water to give a slurry called milk of lime, which is then carbonated by bubbling CO_2 through it. The reactions involved in the process are as follows:



The crystal sizes required for various commercial applications may be controlled by temperature, pH, concentrations, and mixing rate.

Calcium carbonate also may be precipitated by mixing solutions of calcium chloride and sodium carbonate.

Reactions

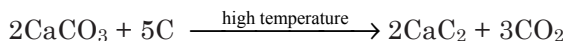
Calcium carbonate decomposes to calcium oxide and CO_2 on heating. Treatment with dilute mineral acids produces corresponding calcium salts with liberation of CO_2 :



In the presence of CO_2 it dissolves in water with the formation of bicarbonate:



It is reduced to calcium carbide when heated with coke or anthracite in an electric furnace:



Analysis

Elemental composition: Ca 40.04%, C 12.00%, O 47.96%. CaCO_3 dissolves in water in the presence of a few drops of HCl. The solution is analyzed for calcium by AA or ICP spectroscopy or by treatment with ammonium oxalate followed by titration with potassium permanganate.

CALCIUM CARBIDE

[75–20–7]

Formula: CaC_2 ; MW 64.100

Uses

The most important application of calcium carbide is the production of acetylene. It also is used to produce calcium cyanamide, CaCN_2 , a nitrogen fertilizer and a source of ammonia.

Physical Properties

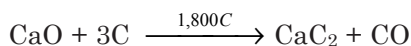
Grayish-black orthorhombic crystal; density 2.22 g/cm³; melts at 2,200°C; reacts with water.

Thermochemical Properties

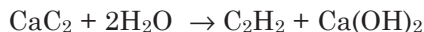
ΔH_f°	-14.29 kcal/mol
ΔG_f°	-15.51 kcal/mol
S°	16.73 cal/degree mol
C_p	14.99 cal/degree mol

Preparation

Calcium carbide is produced by the reaction of calcium oxide with carbon in an electric furnace at temperatures in the range 1,800° to 2,100°C:

**Reactions**

Calcium carbide reacts with water producing acetylene:



Reaction with nitrogen at elevated temperatures produces calcium cyanamide, used as a fertilizer:

**Analysis**

Elemental composition: Ca 62.53%, C 37.48%. The compound can be determined by various x-ray techniques.

Hazard

Contact with water can be hazardous due to the formation of acetylene which is highly flammable.

CALCIUM CHLORIDE

[10043-52-4]

Formula: CaCl_2 ; MW 110.99; also forms mono-, di-, tetra- and hexahydrates; $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ [22691-02-7], $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ [10035-04-8], $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ [25094-02-4] and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ [7774-34-7], respectively.

Occurrence and Uses

Calcium chloride may be found in nature as the mineral tachhydrite, $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$. It also is found in other minerals. Its concentration in sea water is about 0.15%.

Calcium chloride has several industrial applications. The major applications of this compound are in deicing of roads, dust control, imparting stability to roads and buildings, and to improve traction in tractor tires. It is mixed with ice to make freezing mixtures. Hexahydrate mixed with crushed ice can lower the temperature of the cooling bath to below -50°C . It also is used as a desiccant for dehydrating gases and liquids. It is added to cement in various proportions to manufacture different types of concrete. Other uses are in adhesives, to lower gel temperatures, and as a calcium source in liquid feed supplements for dairy cattle. Also, the compound is used to control particle size development and reduce coalescence in plastics.

Physical Properties

White crystal, powder or flake; highly hygroscopic; the compound and its solutions absorb moisture from the air at various rates depending on calcium chloride concentrations, relative humidity and vapor pressure of water in the air, temperature, surface area of exposed material, and the rate of air circulation; at 40% and 95% relative humidity and 25°C , one gram anhydrous calcium chloride may absorb about 1.4 g and 17 g water, respectively. (Shearer, W. L. 1978. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., vol. 4, pp. 432–6. New York: Wiley Interscience); density 2.15, 2.24, 1.85, 1.83 and 1.71 g/cm^3 for the anhydrous salt and its mono-, di-, tetra- and hexahydrates, respectively; anhydrous salts melts at 772°C , while the mono-, di-, tetra- and hexahydrates decompose at 260° , 175° , 45.5° and 30°C , respectively; the anhydrous salt vaporizes at $1,935^{\circ}\text{C}$; highly soluble in water, moderate to high solubility in alcohol.

Thermochemical Properties

$\Delta H_f^{\circ} (\text{CaCl}_2)$	-190.11 kcal/mol
$\Delta H_f^{\circ} (\text{CaCl}_2 \cdot \text{H}_2\text{O})$	-265.53 kcal/mol
$\Delta H_f^{\circ} (\text{CaCl}_2 \cdot 2\text{H}_2\text{O})$	-335.56 kcal/mol
$\Delta H_f^{\circ} (\text{CaCl}_2 \cdot 4\text{H}_2\text{O})$	-480.40 kcal/mol
$\Delta H_f^{\circ} \text{CaCl}_2 \cdot 6\text{H}_2\text{O})$	-623.33 kcal/mol
$\Delta G_f^{\circ} (\text{CaCl}_2)$	-178.97 kcal/mol
$S^{\circ} (\text{CaCl}_2)$	$25.91\text{ cal/degree mol}$
$C_p (\text{CaCl}_2)$	$17.42\text{ cal/degree mol}$
$C_p (\text{CaCl}_2 \cdot \text{H}_2\text{O})$	$25.39\text{ cal/degree mol}$
$C_p (\text{CaCl}_2 \cdot 2\text{H}_2\text{O})$	$41.33\text{ cal/degree mol}$
$C_p (\text{CaCl}_2 \cdot 4\text{H}_2\text{O})$	$60.03\text{ cal/degree mol}$
$C_p (\text{CaCl}_2 \cdot 6\text{H}_2\text{O})$	$71.87\text{ cal/degree mol}$
$\Delta H_{\text{fus}} (\text{CaCl}_2)$	6.82 kcal/mol
$\Delta H_{\text{fus}} (\text{CaCl}_2 \cdot \text{H}_2\text{O})$	4.13 kcal/mol
$\Delta H_{\text{fus}} (\text{CaCl}_2 \cdot 2\text{H}_2\text{O})$	3.09 kcal/mol
$\Delta H_{\text{fus}} (\text{CaCl}_2 \cdot 4\text{H}_2\text{O})$	7.13 kcal/mol
$\Delta H_{\text{fus}} (\text{CaCl}_2 \cdot 6\text{H}_2\text{O})$	10.94 kcal/mol
$^*\Delta H_{\text{soln}} (\text{CaCl}_2)$	-174 kcal/mol
$^*\Delta H_{\text{soln}} (\text{CaCl}_2 \cdot \text{H}_2\text{O})$	-96.8 kcal/mol
$^*\Delta H_{\text{soln}} (\text{CaCl}_2 \cdot 2\text{H}_2\text{O})$	-72.8 kcal/mol

$^*\Delta H_{\text{soln}} (\text{CaCl}_2 \cdot 4\text{H}_2\text{O})$	-14.2 kcal/mol
$^*\Delta H_{\text{soln}} (\text{CaCl}_2 \cdot 6\text{H}_2\text{O})$	17.2 kcal/mol

* to infinite dilution in water.

Preparation

Calcium chloride is obtained as a by-product in the manufacture of sodium carbonate (soda ash) by ammonia-soda (Solvay) process. The process involves the reaction of sodium chloride with calcium carbonate and ammonia. Calcium chloride is currently produced in bulk amounts by evaporation of natural underground brines. In the laboratory, calcium chloride can be prepared by treating limestone with hydrochloric acid followed by evaporation of solution to obtain crystals. The crystals are dehydrated to obtain anhydrous salt. Calcium oxide or hydroxide may be used instead of carbonate.

Reactions

In aqueous solutions, calcium chloride undergoes double decomposition reactions with a number of soluble salts of other metals to form precipitates of insoluble calcium salts. For example, mixing solutions of calcium chloride with sodium carbonate, sodium tungstate and sodium molybdate solutions precipitates the carbonates, tungstates, and molybdates of calcium, respectively. Similar precipitation reactions occur with carboxylic acids or their soluble salt solutions. CaCl_2 forms calcium sulfide when H_2S is passed through its solution. Reaction with sodium borohydride produces calcium borohydride, $\text{Ca}(\text{BH}_4)_2$. It forms several complexes with ammonia. The products may have compositions $\text{CaCl}_2 \cdot 2\text{NH}_3$, $\text{CaCl}_2 \cdot 4\text{NH}_3$, and $\text{CaCl}_2 \cdot 8\text{NH}_3$.

Analysis

Elemental composition: Ca 36.11%, Cl 63.89%. An aqueous solution of the compound may be acidified and analyzed for calcium by AA or ICP methods (see Calcium). The solution may be analyzed for chloride ion by ion selective electrode, ion chromatography or by argentometric titration.

CALCIUM CYANAMIDE

[156-62-7]

Formula: CaCN_2 ; MW 80.11; cyanamide ion is linear and structurally similar to CO_2 ; Structure $\text{N} \equiv \text{CN} = \text{Ca}$

Synonyms: calcium carbimide; lime nitrogen; nitrolime

Uses

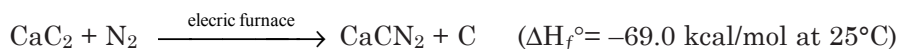
Calcium cyanamide is used primarily as a fertilizer. It also is used as a defoliant and pesticide. Other major applications of this compound are in hardening iron and steel, and in preparation of calcium cyanide and melamine.

Physical Properties

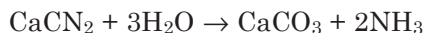
Pure product is a colorless, hexagonal crystal or white powder. Commercial grade material may be grayish-black powder or lump (the color is due to presence of calcium carbide and other impurities); density 2.29 g/cm³; melts around 1,340°C; sublimes around 1,150 to 1,200°C on rapid heating; reacts with water.

Preparation

Calcium cyanamide is prepared from calcium carbide. The carbide powder is heated at about 1,000°C in an electric furnace into which nitrogen is passed for several hours. The product is cooled to ambient temperatures and any unreacted carbide is leached out cautiously with water.

**Reactions**

Calcium cyanamide partially hydrolyzes to calcium hydrogen cyanamide, CaHCN₂. The final hydrolysis products are calcium carbonate and ammonia. The reaction is slow, occurring in moist soil:



When heated at elevated temperatures in oxygen (or air) it oxidizes to calcium oxide, carbon dioxide and oxides of nitrogen.

Analysis

Elemental composition: Ca 50.03%, C 14.99%, N 34.98. A measured amount of the compound is hydrolyzed with water. The product CaCO₃ is filtered, dried and determined by gravimetry. Calcium carbonate or the parent calcium cyanamide may be digested with nitric acid, diluted appropriately, and analyzed for Ca by AA or ICP spectroscopy. The hydrolysis product in solution, ammonia, may be measured by ammonium ion selective electrode, or by colorimetry followed by Nesslerization.

CALCIUM FLUORIDE

[7789-75-5]

Formula: CaF₂; MW 78.075

Occurrence and Uses

Calcium fluoride occurs in nature as the mineral fluorspar or fluorite. It is used as a flux in ferrous metallurgy to enhance the fluidity of the slag. An important application of this compound is in the manufacture of fluorine and hydrofluoric acid, starting materials for producing many fluoroorganics. It also is used in glass and ceramics. Pure crystals are used in lasers, optics, and electronics. Other applications are in high temperature, dry-film lubricants;

catalysis, and fluoridation of drinking water.

Physical Properties

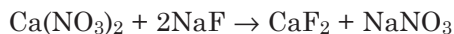
White cubic crystal or powder; refractive index 1.434; density 3.18 g/cm³; hardness 4 Mohs; melts at 1,418°C; vaporizes at 2,533°C; insoluble in water (16 mg/L at 20°C); K_{sp} 3.9×10^{-11} ; slightly soluble in dilute mineral acid; soluble in concentrated acids (with reaction).

Thermochemical Properties

ΔH_f°	−293.5 kcal/mol
ΔG_f°	−281.0 kcal/mol
S°	16.37 cal/degree mol
C_p	16.01 cal/degree mol
ΔH_{fus}	7.1 kcal/mol

Production

The commercial product is obtained from naturally occurring mineral fluorspar, which is purified and powdered. Also, it may be precipitated by mixing a solution of sodium fluoride with a soluble calcium salt:

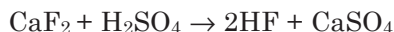


Alternatively, it may be obtained by treating calcium carbonate with hydrofluoric acid:



Reactions

Reaction with concentrated sulfuric acid yields hydrogen fluoride and calcium sulfate:



Similar HF liberation occurs with other concentrated mineral acids.

Analysis

Elemental composition: Ca 51.33%, F 48.67%. The compound may be analysed nondestructively by x-ray techniques. Calcium may be measured in acid extract by AA or ICP spectrophotometry. The insoluble salt is digested in concentrated nitric acid and the acid extract diluted for analysis.

CALCIUM HYDRIDE

[7789–78–8]

Formula: CaH_2 ; MW 42.094

Uses

Calcium hydride is used as a source of hydrogen, liberating hydrogen either on heating or shaking in water. When mixed in water, 1 g calcium hydride would release 1.16 L hydrogen at NTP or about twice the volume of hydrogen generated from equivalent mass of calcium metal in water. Other applications are in organic synthesis as a reducing agent to reduce metal oxides to metals, and as a drying agent.

Physical Properties

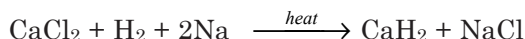
Grayish orthorhombic crystal or powder; stable at ambient temperature; density 1.70 g/cm³; melts at 816°C; reacts with water and alcohol.

Thermochemical Properties

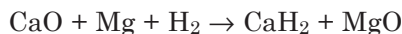
ΔH_f°	-43.38 kcal/mol
ΔG_f°	-34.06 kcal/mol
S°	9.89 cal/degree mol
C_p	9.80 cal/degree mol

Preparation

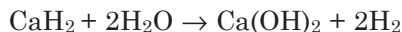
Calcium hydride may be prepared from its elements by direct combination of calcium and hydrogen at 300 to 400°C. It also can be made by heating calcium chloride with hydrogen in the presence of sodium metal:



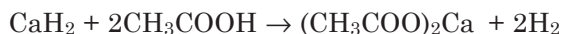
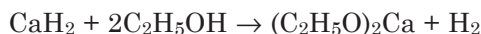
Alternatively, calcium hydride may be prepared by the reduction of calcium oxide with magnesium in the presence of hydrogen:

**Reactions**

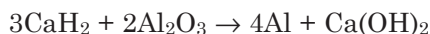
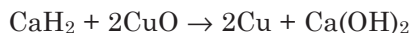
Calcium hydride reacts with water, evolving hydrogen:



Similar reaction occurs with lower alcohols and carboxylic acids:

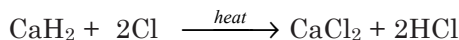


Calcium hydride is a strong reducing agent. It reduces most metal oxides to metals:



When heated with chlorine, bromine or iodine, the reaction goes to incan-

descent with the formation of calcium halide and hydrogen halide:



Analysis

Elemental composition: Ca 95.41%; H 4.79%. A measured amount of the solid is carefully treated with water and the volume of evolved hydrogen is measured using a manometer (1g liberates 1.16 L H₂ at NTP). The solution is then acidified with nitric acid and diluted for the measurement of calcium by AA or ICP spectrophotometry, or by a wet method (see Calcium). The liberated hydrogen gas may be analyzed by GC using a TCD. Many packed and capillary GC columns are commercially available.

Hazard

Calcium hydride ignites in air on heating and can explode violently if mixed and rubbed with a strong oxidizing agent such as perchlorate or bromate. Contact with water produces hydrogen which can create a fire hazard in a confined space.

CALCIUM HYDROXIDE

[1305-62-0]

Formula: Ca(OH)₂; MW 74.093

Synonyms: hydrated lime; slaked lime; calcium hydrate

Uses

Calcium hydroxide has wide industrial applications. It is used to make cement, mortar, plaster, and other building materials. It also is used in water soluble paints, and for fireproofing coatings and lubricants. Other applications are in the manufacture of paper pulp; as a preservative for egg; in vulcanization of rubber; as a depilatory for hides; and in preparation of many calcium salts.

Physical Properties

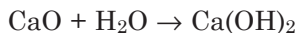
Soft white crystalline powder; hexagonal; density 2.34 g/cm³; slightly bitter taste; loses water when heated at elevated temperatures (580°C); slightly soluble in water; K_{sp} 1.2×10⁻¹⁴; aqueous solution alkaline; soluble in glycerol and acids; insoluble in alcohol.

Thermochemical Properties

ΔH _f [°]	-235.47 kcal/mol
ΔG _f [°]	-214.51 kcal/mol
S [°]	19.93 cal/degree mol
C _p	20.90 cal/degree mol

Production

Calcium hydroxide is produced commercially by treating lime with water:



In the laboratory it may be prepared by treating an aqueous solution of any calcium salt with an alkali.

Reactions

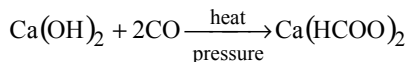
Calcium hydroxide on heating at 580°C loses its water, forming calcium oxide (CaO). Ca(OH)₂ forms calcium carbonate by absorbing CO₂ from air or when CO₂ is passed through a suspension in water. Reaction with sulfuric acid yields calcium sulfate dihydrate:



Mixing with other mineral acids following crystallization or evaporation of solution produces corresponding calcium salts.

It combines with sulfur dioxide to form calcium sulfite hemihydrate, CaSO₃ · ½H₂O which can oxidize in air in the presence of moisture to give calcium sulfate dihydrate, CaSO₄ · 2H₂O. However, when SO₂ is passed through a solution of calcium hydroxide, calcium bisulfite, Ca(HSO₃)₂ is obtained. The solution is yellowish when it contains bisulfite in aqueous SO₂.

When heated with carbon monoxide under pressure, the product is calcium formate, Ca(HCOO)₂:



Hot aqueous solution of calcium hydroxide and iodine react in the presence of chlorine to form calcium iodate, Ca(IO₃)₂.

Analysis

Elemental composition: Ca 54.09%, H 2.72%, O 43.19%. Calcium may be measured by atomic absorption or emission spectroscopy (see Calcium). Its concentration in its alkaline aqueous solution may be measured by acid-base titration.

CALCIUM HYPOCHLORITE

[7778-54-3]

Formula: Ca(OCl)₂; MW 142.99

Synonym: calcium oxychloride

Uses

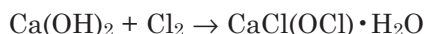
Calcium hypochlorite is used as a disinfectant and bactericide. It also is used as a fungicide; a deodorant; an oxidizing agent; and as a bleaching agent for paper and textiles. Some other applications of this compound are in refining sugar and producing chlorine.

Physical Properties

White crystalline solid; density 2.35 g/cm³; decomposes when heated to 100°C; soluble in water and alcohol (with decomposition).

Preparation

Calcium hypochlorite may be prepared by passing chlorine into a slurry of lime and sodium hydroxide. Alternatively, chlorine is passed into a solution of hydrated lime to produce bleaching powder, $\text{CaCl}(\text{OCl}) \cdot \text{H}_2\text{O}$:



The bleaching powder solution is then treated with sodium chloride to salt out calcium hypochlorite. The product obtained in its dihydrate form is dried under vacuum.

The commercial grade material usually contains 50 to 70% calcium hypochlorite.

Reactions

Calcium hypochlorite is an oxidizing agent. It undergoes vigorous to violent reactions with reducing agents and organics. In aqueous solution, it dissociates to calcium and hypochlorite ions. The hypochlorite ions form hypochlorous acid and molecular chlorine, which coexist in equilibrium.

Analysis

Elemental composition: Ca 28.03%, Cl 49.59%, O 22.38%. Calcium can be measured by various instrumental techniques or wet methods (see Calcium). Hypochlorite ion may be analyzed by ion chromatography. Free chlorine (as Cl_2) in the aqueous solution may be measured by DPD colorimetry or by iodometric titration (see Chlorine).

CALCIUM NITRATE

[10124–37–5]

Formula: $\text{Ca}(\text{NO}_3)_2$; MW 164.09; also forms a tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

[13477–34–4]

Synonyms: lime nitrate; lime saltpeter; Norwegian saltpeter, nitrocalcite

Uses

Calcium nitrate is used in explosives, matches and pyrotechnics. Other applications are in the manufacture of incandescent mantle; and as an additive to diesel fuel for corrosion inhibition.

Physical Properties

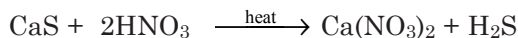
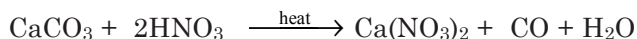
White cubic crystal; hygroscopic; density 2.50g/cm³; melts at 561°C; highly soluble in water; also dissolves in alcohols and acetone.

Thermochemical Properties

ΔH_f°	-244.24 kcal/mol
ΔG_f°	-177.53 kcal/mol
S°	46.18 cal/degree mol
C_p	35.71 cal/degree mol

Preparation

Calcium nitrate may be prepared by the reaction of nitric acid with calcium carbonate or calcium sulfide:

**Analysis**

Elemental composition: Ca 24.42%, N 17.07%, O 58.50%. Calcium ion in its aqueous solution may be measured by various instrumental techniques or titrimetry (see Calcium). Nitrate ion can be measured by ion-chromatography or using a nitrate ion-selective electrode. The aqueous solutions must be diluted appropriately for such measurements.

Hazard

Calcium nitrate is a strong oxidizing agent. Mixing with organic substances such as fuel oil or hydrocarbons or other oxidizable compounds can cause explosion.

CALCIUM OXIDE

[1305-78-8]

Formula: CaO; MW 56.077

Synonyms: quicklime; lime; burnt lime; unslaked lime; fluxing lime

Uses

Calcium oxide is one of the most important industrial chemicals. It is used in the manufacture of building and construction materials, including bricks, mortar, stucco and plaster. It also is used as a flux in the manufacture of steel.

Other important products made from application of calcium oxide in their manufacturing processes include glass, pulp and paper, aluminum and magnesium. Some other major applications of this compound are in flotation of non-ferrous ores; removal of phosphate and pH control in sewage treatment; neutralization of acid waste effluents; depilatory for hides; drilling fluids; refining cane and beet sugar; in pesticides and fungicides; and as an absorbent for carbon dioxide in the form of soda-lime (a mixture with caustic soda). Also, calcium oxide is used to produce sodium carbonate (Solvay process) and many calcium compounds. Its slaked form, known as slaked lime, $\text{Ca}(\text{OH})_2$ has numerous industrial applications (see Calcium Hydroxide).

Before the advent of electricity, calcium oxide was used to produce the so-called "lime light" to spotlight or illuminate the stage. When heated by an oxygen-hydrogen flame, it incandesces emitting bright white light.

Physical Properties

Gray-white granular powder or lumps; cubic crystals; density 3.34 g/cm^3 ; melts at $2,572^\circ\text{C}$; becomes incandescent when heated to its melting point; vaporizes at $2,850^\circ\text{C}$; soluble in water forming slaked lime; also soluble in acids with decomposition; practically insoluble in alcohol.

Thermochemical Properties

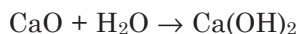
ΔH_f°	-151.74 kcal/mol
ΔG_f°	-144.19 kcal/mol
S°	$9.11 \text{ cal/degree mol}$
C_p	$10.04 \text{ cal/degree mol}$
ΔH_{fus}	14.1 kcal/mol

Production

Calcium oxide is commercially obtained from limestone. The carbonate is roasted in a shaft or rotary kiln at temperatures below $1,200^\circ\text{C}$ until all CO_2 is driven off. The compound is obtained as either technical, refractory or agricultural grade product. The commercial product usually contains 90 to 95% free CaO . The impurities are mostly calcium carbonate, magnesium carbonate, magnesium oxide, iron oxide and aluminum oxide.

Reactions

Calcium oxide reacts with water forming calcium hydroxide:

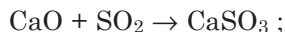


The reaction is highly exothermic, with powdered material.

CaO absorbs CO_2 forming calcium carbonate:

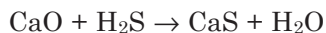


With sulfur dioxide, calcium sulfite is the product which slowly oxidizes to calcium sulfate:

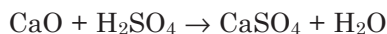


172 CALCIUM PHOSPHATE, DIBASIC

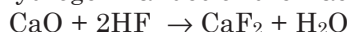
and with hydrogen sulfide the product is calcium sulfide:



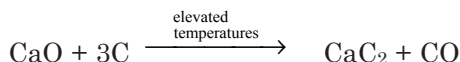
Reactions with acids give corresponding calcium salts:



and with hydrogen halides or their acids, calcium halide is formed:



When pulverized calcium oxide is heated with carbon (crushed coke or anthracite) in an electric furnace, calcium carbide is produced:



Analysis

Elemental composition: Ca 71.47%, O 28.53%. Acidified CaO solution may be analyzed for Ca by flame AA or ICP spectrometry (see Calcium). The oxide may be determined by x-ray techniques. The compound may be identified by adding a small quantity slowly and carefully to water (reaction may be violent) and testing the pH (pH should be alkaline). Passage of CO_2 into its clear solution should turn the solution milky due to formation of CaCO_3 .

Hazard

Skin contact of the powder can cause severe irritation. Mixing the powder form of the compound with water can produce explosive reactions with liberation of large quantities of heat. The reaction occurs after a few minutes delay (Mellor, J. W. 1941. *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 3, pp. 673. London: Longmans Green). The presence of moisture in storage containers or bottles may produce an explosion hazard. Hydration of granular lumps, however, is slow and smooth.

CALCIUM PHOSPHATE, DIBASIC

[7757-93-9]

Formula: CaHPO_4 ; MW 136.06; also occurs as dihydrate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [7789-77-7] known as brushite.

Synonyms: calcium hydrogen phosphate; secondary calcium phosphate; bicalcium phosphate

Uses

Dibasic calcium phosphate is found in nature as the mineral monetite. It is used as a food supplement and source of calcium, both in human food and ani-

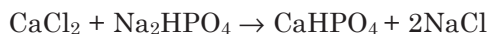
mal feed. It is used in dough conditioner; in several dental products and in medicine. Other applications are in fertilizers, plastics and in the manufacture of glass.

Physical Properties

White triclinic crystal; density 2.92 g/cm³ (anhydrous) and 2.31 g/cm³ (dihydrate); hardness 3.5 Mohs; decomposes on heating; insoluble in water and alcohol; K_{sp} 2.7×10^{-7} ; soluble in dilute mineral acid.

Preparation

Dibasic calcium hydrogen phosphate may be prepared by several methods. It is precipitated by mixing solutions of calcium chloride and disodium hydrogen phosphate:



It also is prepared by treating phosphoric acid with lime water (suspension of calcium hydroxide in water). Also, it is obtained as a by-product in the preparation of hydroxyapatite. The preparation involves the reaction of phosphoric acid with calcium phosphate.



Analysis

Elemental composition: Ca 29.46%, H 0.74%, P 22.77%, O 47.04%. The compound may be identified by x-ray analysis. Calcium may be analyzed by AA or ICP spectrometry in aqueous matrix following acid digestion. Phosphorus in the aqueous solution may be determined by colorimetry (see Phosphorus).

CALCIUM PHOSPHATE, MONOBASIC

[7758-23-8]

Formula: $\text{Ca}(\text{H}_2\text{PO}_4)_2$;

MW 234.06; readily forms monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

Synonyms: monocalcium orthophosphate; calcium biphosphate; primary calcium phosphate, calcium dihydrogen phosphate.

Uses

Monobasic calcium phosphate is primarily used in fertilizers. It also is used in baking powders; as a mineral supplement in food; as a buffer for pH control; and as a stabilizer for plastics.

Physical Properties

Colorless shiny crystals, granules or powder; the impure material is hygroscopic due to the presence of trace phosphoric acid and other impurities; acid

taste; density (monohydrate 2.22 g/cm³); monohydrate loses water at 100°C; decomposes at 200°C; moderately soluble in water; aqueous solution acidic; soluble in dilute mineral acids and acetic acid.

Preparation

Monobasic calcium phosphate may be prepared in the laboratory by the reaction of calcium carbonate with phosphoric acid:



Fertilizer grade product is obtained by pulverized phosphate rock (tricalcium phosphate) in phosphoric or sulfuric acid and evaporating the solution.

Analysis

Elemental composition: Ca 17.12%, H 1.72%, P 26.47%, O 54.69%

Calcium may be analyzed by AA or ICP spectrophotometry. Its aqueous solution may be analyzed for phosphorus by colorimetry (see Phosphorus).

CALCIUM PHOSPHATE, TRIBASIC

[7758-87-4]

Formula: $\text{Ca}_3(\text{PO}_4)_3$; MW 310.20

Synonyms: calcium orthophosphate; calcium phosphate; tricalcium phosphate; tertiary calcium phosphate; precipitated calcium phosphate; bone ash (technical product).

Occurrence and Uses

Tribasic calcium phosphate occurs in nature as minerals, oxydapatite, whitlockite, voelicherite, apatite, phosphorite. It has many industrial applications. Some are similar to the monobasic and dibasic salts. It is used in fertilizers, dental products, ceramics and polishing powder. Some other important applications are in plastics as a stabilizer; as an anticaking agent; as a nutrient supplement in cattle food; for clarifying sugar syrup; as a mordant in dyeing textiles; and as a buffer to control pH.

Physical Properties

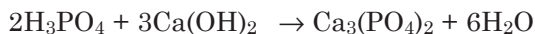
White amorphous powder; refractive index 1.63; density 3.14 g/cm³; melts at 1,670°C; insoluble in water; $K_{\text{SP}} 1.0 \times 10^{-25}$; soluble in acids.

Thermochemical Properties

ΔH_f°	−984.9 kcal/mol
ΔG_f°	−928.5 kcal/mol
S°	56.4 cal/degree mol
C_p	54.4 cal/degree mol

Preparation

Tribasic calcium phosphate is obtained from naturally occurring minerals for fertilizer applications. The compound may be prepared in the laboratory by the reaction of sodium phosphate with calcium chloride with excess of ammonia. Also, it can be prepared by treatment of calcium hydroxide with phosphoric acid:



Analysis

Elemental composition: Ca 38.76%, P 19.97%, O 41.26%. Calcium may be analyzed by AA, and ICP, or x-ray methods (see Calcium). The orthophosphate anion may be analyzed by colorimetry (see Phosphorus). For colorimetric analysis the insoluble tribasic phosphate must be brought into aqueous phase by dissolving in dilute sulfuric acid.

CALCIUM SULFATE

[7778–18–9]

Formula: CaSO_4 ; MW 136.14; also forms hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ [10034–76–1] and the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [10101–41–4].

Synonyms: *anhydrous calcium sulfate*-anhydrite; muriacite; karstenite; anhydrous gypsum; anhydrous sulfate of lime *hemihydrate*-plaster of Paris; annalin; dried gypsum; dried calcium sulfate *dihydrate*-gypsum; alabaster; satin spar; mineral white; terra alba; satinite; light spar; selenite; precipitated calcium sulfate; native calcium sulfate

Occurrence

Both the anhydrous calcium sulfate and dihydrate occur in nature, the former as the mineral, anhydrite, and the latter as gypsum. Gypsum is widely distributed in nature. It has been known since ancient times.

Uses

All three forms of calcium sulfate have many important commercial applications. The anhydrous salt, as insoluble anhydrite, is used in cement and as a paper filler. The soluble anhydrite, highly efficient in absorbing moisture, is commonly used as a desiccant for drying gases and liquids. It is known under the trade name Drierite. The most useful form of calcium sulfate, however, is gypsum. It is used in Portland cement, plaster for walls (gypsum plasters), wall boards, blocks, and mortars. It also is used in agriculture for conditioning soil. Gypsum also is used to produce other calcium compounds.

Hemihydrate is commonly used as plaster of Paris in numerous applications. It is used to make gypsum wallboards, molding plasters and pottery plasters. Pottery plasters are used in ceramics, pottery, and artworks.

Plasters made from hemihydrate also find applications in many orthopedic and dental materials and sanitary wares.

Physical Properties

Anhydrous calcium sulfate is a crystalline substance; orthorhombic; the color may vary as white, gray, blue or brick-red; occurs as insoluble anhydrite or porous soluble anhydrite; density 2.96 g/cm³; hardness 3.5 Mohs; insoluble anhydrite is practically insoluble in water (0.21% at 20°C); soluble anhydrite readily absorbs moisture and is soluble in water.

Hemihydrate is a white fine powder; sparingly soluble in water (3g/L at 25°C); combines with water, setting to a hard mass.

Dihydrate may occur as lumps or powder; density 2.32 g/cm³; partially loses water on heating at 100°C; slightly soluble in water (2.4 g/L at 25°C); $K_{SP} = 2.4 \times 10^{-5}$; almost insoluble in organic solvents.

Thermochemical Properties

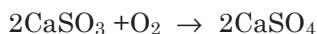
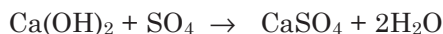
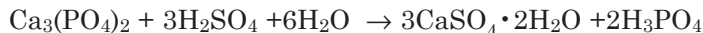
ΔH_f° (anhydrite)	-342.76 kcal/mol
ΔG_f° (anhydrite)	-315.93 kcal/mol
S° (anhydrite)	25.50 cal/degree mol
C_p (anhydrite)	23.82 cal/degree mol
ΔH_f° (hemihydrate)	-376.85 kcal/mol
ΔG_f° (hemihydrate)	-343.41 kcal/mol
S° (hemihydrate)	31.20 cal/degree mol
C_p (hemihydrate)	28.54 cal/degree mol
ΔH_f° (dihydrate)	-483.42 kcal/mol
ΔG_f° (dihydrate)	-429.60 kcal/mol
S° (dihydrate)	46.40 cal/degree mol
C_p (dihydrate)	44.46 cal/degree mol

Manufacture

Gypsum may be produced from the natural mineral by surface quarrying or mining from natural deposits. Natural gypsum is generally found to contain both the anhydrous and dihydrate forms together. Also, it contains a number of impurities, such as, clay, silica, limestone, and magnesium carbonate. The rock is crushed to size as required and calcined. The dihydrate is dehydrated to hemihydrate or anhydrite. The calcination usually is done in a steel cylindrical vessel known as a kettle for several hours under hot air flow at temperatures ranging between 100 to 125°C. Calcination may be carried out under steam pressure. Soluble anhydrite may be produced by further heating the calcined product at temperatures between 200 to 220°C, and may be obtained in fine powder or granule form. Insoluble anhydrite may be produced in a similar manner, however, by calcination over a longer time period. Temperature controls and rate of heating are crucial factors in the manufacture of various forms of calcium sulfate.

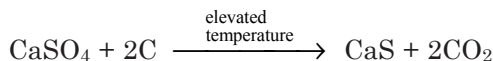
Calcium sulfate also is manufactured by various synthetic reactions. The

products, generally known as synthetic gypsums, may be obtained as dihydrate or hemihydrate. Many commercial plants operate on synthetic routes to produce calcium sulfate. It is produced by the reaction of a calcium salt with sulfuric acid or sulfur dioxide:

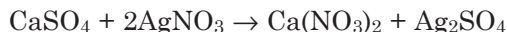


Reactions

Calcium sulfate exhibits high thermal stability. At elevated temperatures, it occurs in anhydrous form. The dihydrate loses its water molecules upon strong heating. When ignited with charcoal, it is reduced to calcium sulfide:



In aqueous solution, the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (soluble in water) undergoes double decomposition reactions with other soluble salts, precipitating out insoluble salts:



Analysis

Elemental composition: Ca 29.44%, S 23.55%, O 47.01%. The compound may be digested with nitric acid and the acid extract may be analyzed for Ca by AA or ICP spectrophotometry. Various x-ray techniques may be applied for the nondestructive identification of the compound. Water of crystallization may be determined by gravimetry following high temperature heating to expel all water from the hydrated crystals.

CALCIUM SULFIDE

[20548–54–3]

Formula: CaS ; MW 72.144

Occurrence and Uses

Calcium sulfide occurs in nature as the mineral oldhamite. It has several applications. The 'luminous' calcium sulfide is used in phosphors, luminous paints and varnishes. Calcium sulfide also is used as an additive to lubricants; and as a flotation agent in ore extraction.

Physical Properties

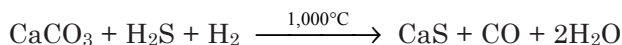
Pure compound is white cubic crystal or powder; impure or luminous calcium sulfide is pale yellow to light gray; bitter taste; odor of H_2S in moist air; hygroscopic; refractive index 2.137; hardness 4.0 Mohs; density 2.59 g/cm^3 ; melts at $2,525^\circ\text{C}$; slightly soluble in water; insoluble in alcohol; soluble in acids with decomposition.

Thermochemical Properties

ΔH_f°	-115.30 kcal/mol
ΔG_f°	-114.10 kcal/mol
S°	13.50 cal/degree mol
C_p	11.33 cal/degree mol

Preparation

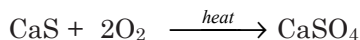
Crude calcium sulfide may be obtained by ignition of pulverized calcium sulfate with charcoal. The products also may contain calcium carbonate, sulfite, carbonaceous ash and unreacted calcium sulfate. In the laboratory, pure calcium sulfide may be prepared by heating pure calcium carbonate with hydrogen sulfide and hydrogen at $1,000^\circ\text{C}$:



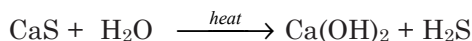
Luminous calcium sulfate is prepared by the ignition of calcium carbonate with sulfur in the presence of small quantities of manganese or bismuth salts.

Reactions

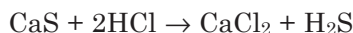
When heated in dry air or oxygen, the compound is oxidized to calcium sulfite and then to the sulfate, CaSO_4 :



Partial decomposition occurs in hot water with the evolution of H_2S :



Reactions with acids evolve H_2S ; evaporation and crystallization of the solutions give corresponding calcium salts:



Vigorous to violent reactions can occur with oxidizing agents, such as potassium chlorate, potassium nitrate or lead dioxide.

Analysis

Elemental composition: Ca 55.56%, S 44.44%. The compound may be identified from the odor of H_2S evolved when mixed with dilute acids. A paper moistened with lead acetate solution and exposed to liberated H_2S turns

black. This is a qualitative test for sulfide. Calcium may be analysed by various instrumental techniques, such as AA or ICP spectroscopy and x-ray techniques. (see Calcium).

CALIFORNIUM

[7440–71–3]

Symbol: Cf; atomic number 98; atomic weight 251 (the principal isotope); californium is a transuranium radioactive actinide element; electron configuration $[\text{Rn}]5f^{10}7s^2$; valence state +3; most stable isotope $^{251}_{98}\text{Cf}$, half-life 800 years; isotope properties are presented below:

isotopes	half-life	decay mode
californium–244	25 min	α –emission
californium–245	44 min	orbital electron capture α –emission
californium–246	35.7 hr.	α –emission
californium–247	2.4 hr.	orbital electron capture
californium–248	350 days	α –emission spontaneous fission
californium–249	360 yr.	α –emission
californium–250	10 yr.	α –emission spontaneous fission
californium–251	800 yr.	α –emission
californium–252	2.55 yr.	α –emission spontaneous fission
californium–253	19 days	positron decay
californium–254	60 days	spontaneous fission

History, Occurrence and Uses

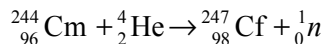
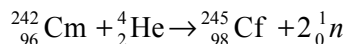
The element was synthesized in 1950 by S. G. Thompson, A. Ghiorso, K. Street, and Glen T. Seaborg. It was named after the state of California. Californium does not occur in nature. It can be synthesized only in microgram amounts in a nuclear reactor. The principal compounds of the element that have been synthesized are the californium trifluoride, CfF_3 ; californium trichloride, CfCl_3 ; californium oxide, Cf_2O_3 ; californium oxychloride $\text{Cf}(\text{OCl})_3$; and californium hydroxide $\text{Cf}(\text{OH})_3$. The element has not yet been obtained in metallic state.

The isotope californium–252 undergoes spontaneous fission generating neutrons. It serves as a convenient source of neutrons for neutron activation analysis, neutron moisture gages, and in the determination of water and oil-bearing layers in well-logging. It is expected to have many other potential applications, including synthesis of other heavy isotopes.

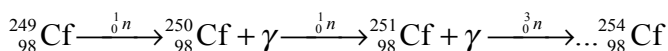
Production

Isotopes of californium may be produced in a cyclotron by neutron irradiation or charged particle bombardment. Lighter isotopes of californium may be produced by bombardment of curium–242 or curium–244 with alpha particles

having 35.5 MeV energy:

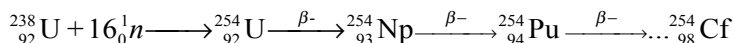
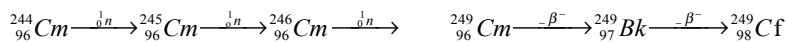


The above method was used for producing californium-245 during its first ever synthesis. Heavier isotopes of californium may be obtained by intense neutron irradiation:



The isotope ${}^{249}_{98}\text{Cf}$ may be obtained by β^- -decay of ${}^{249}_{97}\text{Bk}$.

This, in turn is produced by successive slow neutron irradiation of curium-244: Californium-254 may be produced by thermonuclear explosion resulting in the reaction of uranium-238 with intense neutron flux followed by a sequence of β^- decays (Cunningham, B. B. 1968. In *Encyclopedia of Chemical Elements*, ed. Clifford A. Hampel, New York: Reinhold Book Co.)



Californium is separated from other elements by fractionation and precipitation, and further purified by solvent extraction or ion exchange.

Health Hazard

Exposure to Cf radiation can cause cancer. Similar to other radioactive elements, californium can accumulate in the skeletal system, causing damage to the red cell forming mechanism.

CARBON

[7440-44-0]

Symbol C; atomic number 6; atomic weight 12.011; a Group IV A (Group 14) nonmetal element; atomic radius 0.77Å; electron configuration $1s^2 2s^2 2p^2$; primarily forms tetravalent covalent compounds with linear, triangular (planar) and tetrahedral geometry, with coordination numbers 2, 3, and 4, respectively; electronegativity 2.5; isotopic composition C-12 98.89%, C-13 1.11%; the

beta emitter radioisotope C-14 has a half-life of 5,570 years.

Occurrence

Carbon is probably the most widely distributed element on earth. It is found in all living organisms; in coal, petroleum and natural gases; in numerous rocks as carbonates (limestone, dolomite and marble); in the atmosphere as carbon dioxide; and is the basic elemental constituent of all organic compounds. It forms more compounds (with the exception of hydrogen) than all other elements combined. Carbon and hydrogen together, or additionally in combination with oxygen, nitrogen, sulfur, phosphorus, and halogens form over eight million organic compounds.

Carbon also occurs in abundance in the sun, stars and the atmospheres of planets and their moons. The latter consist of carbon dioxide and methane. Its abundance in the earth's outer crust is estimated to be 0.2%.

Elemental carbon has many important applications. The diamond is a precious gem, known to mankind for ages; graphite is used as an electrode and has numerous other applications; carbon-14 isotope is used in carbon dating; and the isotope carbon-13 in tracer studies and NMR. Carbon black is used in paints, pigments and inks. Activated carbon is used as an adsorbent for purification of water and separation of gases. Coke is used for electrothermal reduction of metal oxides to their metals. These applications are discussed below in more detail.

Allotropy

Carbon exists in three allotropic forms; diamond, graphite, and fullerenes, each distinctly differing from others in physical and chemical properties. Diamond [7782-40-0] is one of the hardest substances known. The Mohs hardness is 10.0, the highest in the scale as Mohs reference standard. Its density 3.513 g/cm³; refractive index 2.417; and melting point about 3,700°C. The carbon atoms in diamonds are arranged in cubic form having stacked layers perpendicular to the diagonals of the cube. Also, the diamond occurs in hexagonal form which is less stable than the cubic form. The hexagonal form of diamond is found in meteorites and can be synthesized.

The diamond is found in natural deposits in many parts of the world. Also, it can be synthesized from graphite or other carbonaceous materials. Graphite can be converted to diamond under high temperatures (about 1,400°C) and very high pressure (in the range 4,000–5,000 atm) in the presence of a metal catalyst such as iron or nickel. Presence of trace impurities can impart different coloration to diamonds. For example, introducing trace boron or nitrogen causes blue or yellow coloration.

Graphite [7440-44-0] is black hexagonal crystal. The hexagonal layer has each carbon atom surrounded by three other carbon atoms. The C–C bond length is 1.415 Å. Each network of hexagonal layer is separated from other superposed layers by a distance of 3.35 Å, and is held by weak van der Waal force. Because of this very weak attractive force between each layer, graphite is very soft—probably one of the softest solids, with high lubricity. Its density is 2.25 g/cm³. Graphite exhibits two manifestations; the stable hexagonal form

that commonly occurs at ambient conditions, and a less stable rhombohedral form.

Fullerenes are polyhedral carbon allotropes consisting of large carbon molecules containing 60 to 120 C atoms. [60] Fullerene or fullerene-C60 is made up of arrays of 60 atoms in a roughly spherical shaped molecule. It has a geometry of truncated icosahedron consisting of 20 hexagons and 12 pentagons. The [120] fullerene is a dumbbell shaped dimer of [60]fullerene. Fullerene-C70 is slightly more stable than [60]fullerene. Many other fullerenes are known that have a different number of total carbon atoms per molecule in their five and six membered fused rings. They are strained molecules with moderate stability. The stability of this class of carbon molecules is relatively much lower than diamond or graphite. They decompose when heated at high temperatures. Their decomposition temperatures vary with the number of C atoms in the molecule and its geometric shape. The decomposition temperature of [60]fullerene, one of the most common fullerenes is 750°C.

Fullerenes are found in soot, charcoal and carbon black. They also occur in many other carbonaceous matters. They have also been detected in some meteorites and interstellar matter. In the laboratory they may be produced by passing high electric current through graphite rods and rapidly evaporating the rod in an atmosphere of helium or other inert gases. The fullerene soots produced are dissolved in an organic solvent and separated on a column. Solvent molecules are removed from the crystal by vacuum sublimation. Such preparative methods primarily yield [60]- and [70]fullerenes, and small amounts of higher clusters.

Fullerenes have potential applications in the preparation of carbon support catalysts and diamond films. They have high electrical conductivity and chemical reactivity.

Carbon also is produced and used in other forms; namely, activated carbon, carbon black, and coke, that have many commercial applications. Structurally they are amorphous forms of carbon belonging to the graphites. Activated carbon or activated charcoal has a highly porous honeycomb-like internal structure and adsorbs many gases, vapors, and colloidal solids over its very large internal surface area. Some of its major applications include purification of water and air, air analysis, waste treatment, removal of sulfur dioxide from stack gases, and decolorization of sugar.

Activated carbon is produced by destructive distillation of carbonaceous substances, such as wood, bones, and nut shells. The carbon obtained from distillation is then heated to 800–900°C with steam or carbon dioxide.

Carbon black includes several forms of artificially prepared carbon, such as furnace black, channel black, lamp black, and animal charcoal. It is a finely divided form of carbon consisting of particles of extremely fine size. It is obtained by partial combustion (in 50% required air) of vapors of heavy oil fraction of crude oil in a furnace; or by thermal cracking of natural gas. Carbon black is used in many abrasion-resistant rubber products including tire treads and belt covers. It also is used in typewriter ribbons, printing inks, carbon paper, and paint pigments. It also can be an absorber for solar energy and UV radiation.

Coke is obtained by destructive distillation or carbonization of bituminous coal, coal-tar pitch and petroleum produced during petroleum cracking. Coke from bituminous coal is used to reduce iron ore in blast furnaces; and to produce synthesis gas. Petroleum coke or that obtained from coal-tar pitch is used in electrolytic reduction of aluminum oxide to aluminum and in the preparation of several metal carbides. .

Thermochemical Properties

ΔH_f° (graphite)	0.0 kcal/mol
ΔH_f° (diamond)	0.45 kcal/mol
ΔH_f° ([60]fullerene)	10.16 kcal/mol
ΔH_f° ([70]fullerene)	9.66 kcal/mol
ΔG_f° (diamond)	0.69 kcal/mol
S° (graphite)	1.36 cal/degree mol
S° (diamond)	0.57 cal/degree mol
C_p (graphite)	2.03 cal/degree mol
C_p (diamond)	1.46 cal/degree mol

CARBON DIOXIDE

[124–38–9]

Formula: CO_2 ; MW 44.009; structure $\text{O}=\text{C}=\text{O}$, linear molecule, bond angle 180°C ; net dipole moment zero.

Occurrence and Uses

Carbon dioxide is found throughout nature. Its concentration in the air is 0.036% by volume. It is the primary component of exhaled air of all animals. It also is the product of oxidation of all carbonaceous matter and an end product of complete combustion. It also is found dissolved in natural waters. It occurs in the earth's crust and in volcanic eruptions.

All plants depend on carbon dioxide and water for their survival, making their food by the process of photosynthesis. Carbon dioxide is found in abundance in the atmospheres of many other planets and their moons throughout the solar system.

Carbon dioxide is a greenhouse gas, which traps the infrared radiation re-radiated back by the earth's surface, causing global warming and, therefore, changing the climate. The CO_2 concentration in the atmosphere over a 30-year period from 1960 to 1990 has increased significantly from about 320 to 356 ppm by volume, which is widely attributed to the growth of industrial and automobile CO_2 emission during this period.

Carbon dioxide has extensive commercial applications. Some important applications of this compound include carbonation of beverages; as a fire extinguishing agent; in the manufacture of carbonates; as dry ice (solid CO_2) for refrigeration; as an aerosol propellant; as a shielding gas for welding; as

an inert atmosphere in preparation and handling of flammable substances; in cloud seeding; in fumigation of rice; to produce harmless smoke on stage; as an antiseptic; and as a supercritical fluid to extract organic pollutants for their analyses.

Physical Properties

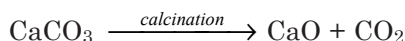
Colorless, odorless and tasteless gas; 1.53 times heavier than air; density 1.80 g/L at 25°C; can be liquefied under pressure; liquefies at -56.6°C at 5.2 atm; density of liquid CO₂ at 0°C and 34 atm 0.914 g/mL; solidifies to white snow-like flakes known as dry ice, density 1.56 g/cm³ at -79°C; dry ice sublimates to CO₂ gas at -78.5°C; critical temperature 31°C; critical pressure 72.79 atm, critical density 94 cm³/mol; moderately soluble in water, solubility 173 mL and 88mL CO₂/100 mL water at 0°C and 20°C, respectively; solubility increases with pressure.

Thermochemical Properties

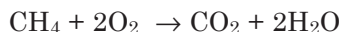
ΔH_f°	-94.05 kcal/mol
ΔG_f°	-94.26 kcal/mol
S°	51.1 cal/degree mol
C_p	8.87 cal/degree mol
ΔH_{fus}	2.156 kcal/mol

Production

Carbon dioxide is produced as a by-product in many processes. It is produced as a by-product in the manufacture of lime from calcium carbonate:

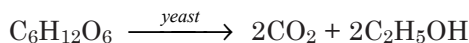


CO₂ also is derived from synthesis gas which is a mixture of CO, CO₂, H₂ and N₂ from air obtained by steam reforming. Carbon dioxide also is obtained by combustion of natural gas:



It also is obtained as a by-product in the Haber-Bosch process for the manufacture of ammonia. The method involves passing steam and air over hot coke.

Carbon dioxide also is produced along with ethanol from fermentation of carbohydrates by yeast:



In the laboratory, CO₂ may be produced by the reaction of any carbonate with a dilute mineral acid:



Reactions

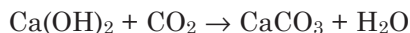
Carbon dioxide is slightly acidic in nature. Its aqueous solution is carbonic acid, H_2CO_3 , a weak unstable acid:



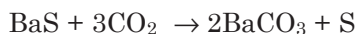
Reactions with alkalis yield carbonates:



It turns lime water milky due to the formation of calcium carbonate:



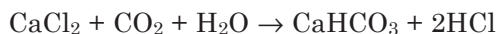
When passed through a solution of alkali or alkaline earth metal sulfide, the corresponding carbonate is produced with deposition of sulfur:



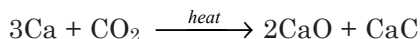
Many metal oxides form carbonates. When passed into an aqueous solution of carbonate, the corresponding bicarbonate is produced:



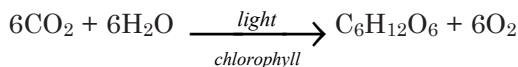
When passed into an aqueous solution of chloride salt of alkali or alkaline earth metal, the product is bicarbonate:



Carbon dioxide reacts with heated calcium metal, forming calcium carbide and calcium oxide:



The photosynthetic conversion of carbon dioxide and water in the presence of sunlight and chlorophyll produces carbohydrates, such as glucose and other sugars, and oxygen:



Analysis

Carbon dioxide may be readily analyzed by various instrumental techniques, such as IR, GC, and GC/MS. Many portable infrared analyzers are available commercially for rapid, on site monitoring of CO_2 . Also, it can be analyzed by GC using a TCD or an FID. It readily may be identified by mass spectrometry from its characteristic ionic mass 44. Dissolved CO_2 in water

may be calculated nomographically from temperature, pH, total dissolved solids, and alkalinity. (APHA, AWWA and WEF.1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, D.C.: American Public Health Association.)

Toxicity

Although CO₂ is nontoxic, exposure to a high concentration can cause asphyxiation due to lack of oxygen. Exposure to 5 to 10% volume in air can be fatal.

CARBON DISULFIDE

[75–15–0]

Formula: CS₂; MW 76.139

Synonym: carbon bisulfide; dithiocarbonic anhydride

Uses

Carbon disulfide is used in the manufacture of rayon, cellophane, electronic vacuum tubes, and xanthogenates. It is used to make carbon tetrachloride. It also is used as an industrial solvent; and as an analytical solvent. Because of its low response to GC-FID, it is used widely in air analysis of organic compounds.

Physical Properties

Colorless liquid; commercial grade has a pungent disagreeable odor, in its purest form the odor is sweet and pleasant; flammable; refractive index 1.6295; density 1.261 g/mL at 20°C; boils at 46.3°C; freezes at –110.8°C; critical temperature 279°C, critical pressure 77.97 atm, critical volume 173 cm³/mol; slightly soluble in water, 0.29 g/100g at 20°C; soluble in alcohol, ether, benzene, chloroform, and oils; forms an azeotrope with water (CS₂: H₂O = 97.2%)

Thermochemical Properties

ΔH_f°	21.44 kcal/mol
ΔG_f°	15.60 kcal/mol
S°	36.17 cal/degree mol
C_p	18.10 cal/degree mol
ΔH_{vap} (at bp)	84.1 cal/g
ΔH_{fus}	1.05 kcal/mol

Preparation

Carbon disulfide is manufactured by heating sulfur vapor with charcoal, and condensing vapors of the compound formed. Alternatively, it may be obtained by heating sulfur with natural gas or petroleum fractions. Instead of sulfur, H₂S may be used. The reaction occurs at very high temperatures. The

product obtained in these reactions may contain sulfur impurities. Carbon disulfide is purified by distillation.

Analysis

Elemental composition: C 15.77%, S 84.23% carbon disulfide. It may be analyzed by GC using a sulfur chemiluminescence detector or by GC/MS. A concentration of 1 ppm in the air may be measured by mass spectrometry. The primary characteristic ionic mass for identification of this compound by mass spectrometry is 76. Many GC columns are available commercially.

Hazard

Carbon disulfide is an extremely flammable liquid, the closed cup flash point being -22°F (-30°C). Its autoignition temperature is 90°C (194°F). Its vapors form explosive mixtures with air, within a wide range of 1.3 to 50.0% by volume in air. Reactions with certain substances can progress to explosive violence. They include finely divided metals, alkali metals, azides, fulminates, and nitrogen dioxide.

The compound is toxic. Repeated inhalation of vapors can produce headache, fatigue, dizziness, nervousness, psychosis, tremors, loss of appetite, and gastric problems. Ingestion of the liquid can be fatal to humans.

CARBON MONOXIDE

[630-08-0]

Formula: CO; MW 28.01

Occurrence and Uses

Carbon monoxide is found in varying concentrations in unventilated and confined spaces resulting from partial oxidation of carbonaceous matter. Burning wood, paper, kerosene, or other organic materials in inadequate air can produce this gas. It also is found in automobile exhaust and tobacco smoke emissions.

Carbon monoxide has many important industrial applications. It is used in Fischer-Tropsch process to produce liquid or gaseous hydrocarbons, synthetic fuels and many oxygenated derivatives. This process was applied before and during World War II to produce synthetic fuels. Probably the most important application of this compound involves production of oxygenated organics in the Synthol process and in oxo synthesis. Many aliphatic alcohols, aldehydes and ketones are produced by catalytic hydrogenation of carbon monoxide. Oxo synthesis produces aldehydes from olefins. Carbon monoxide also is the starting material for preparing metal carbonyls. In metallurgy, it is used as a reducing agent to reduce oxides. In the Mond process it recovers nickel.

Physical Properties

Colorless, odorless and tasteless gas; density 1.229 g/L; very flammable,

burns in air with a bright blue flame; liquefies at -191.5°C ; solidifies at -205°C ; critical temperature -140°C , critical pressure 34.53 atm, critical volume $93\text{ cm}^3/\text{mol}$; soluble in chloroform, acetic acid, ethyl acetate, ethanol, and ammonium hydroxide; sparingly soluble in water ($2.3\text{ mL}/100\text{ mL}$ water at 20°C).

Thermochemical Properties

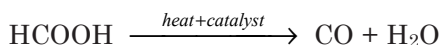
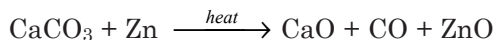
ΔH_f°	-26.41 kcal/mol
ΔG_f°	-32.79 kcal/mol
S°	$47.25\text{ cal/degree mol}$
C_p	$6.96\text{ cal/degree mol}$
ΔH_{fus}	0.198 kcal/mol
ΔH_{vap}	1.44 kcal/mol

Production

Carbon monoxide may be prepared by several methods. Large scale production is carried out by controlled oxidation of natural gas or by the catalytic steam reforming of methane or light petroleum fractions. The products obtained are mixtures of CO, H_2 , and CO_2 . It also is made by gasification of coal and coke with oxygen at about $1,500^{\circ}\text{C}$.

Removal of CO_2 may be achieved by passing the gaseous products through an aqueous base. Alternatively, CO may be recovered by complexing with CuAlCl_4 in benzene or toluene. In pure form it may be prepared by passing a mixture of oxygen and carbon dioxide over incandescent graphite or coke.

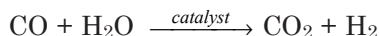
Alternatively, carbon monoxide may be prepared by action of steam either on natural gas or on hot coke or coal. In the laboratory, CO may be produced by heating CaCO_3 with zinc dust; or by dehydration of formic acid:



Reactions

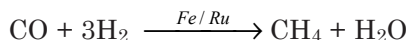
Many CO reactions are industrially important; some of which are outlined briefly below:

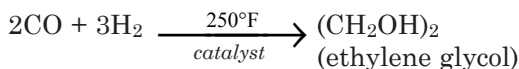
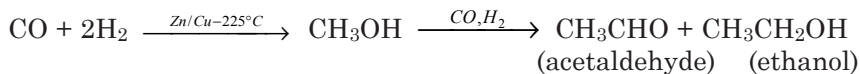
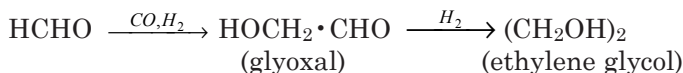
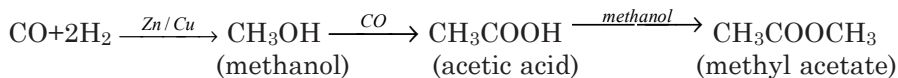
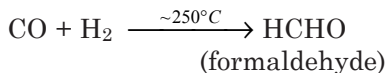
Reaction with steam catalyzed by ZnO–CuO or Fe–Cr yields hydrogen. This reaction, known as “water gas shift,” is a source of industrial hydrogen.



The Fischer-Tropsch reaction involves reduction of CO with H_2 and combination with methanol and olefins in presence of various catalysts to produce an array of oxygenate products of high industrial values.

Reduction with H_2 in the presence of Fe, Ni, or Ru produces methane and other alkanes along with oxygenates.





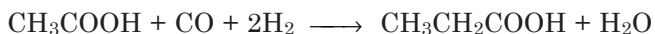
Oxo reaction or hydroformylation reaction involves addition of a hydrogen atom and a formyl group ($-\text{CHO}$) to $\text{C}=\text{C}$ double bond of an olefin making both anti-Markovnikov and Markovnikov products:



Oxo reactions give both linear and branched-chain aldehydes and alcohols.

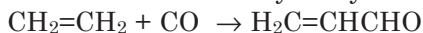
Reppe reaction involves carbonylation of methanol to acetic acid and methyl acetate and subsequent carbonylation of the product methyl acetate to acetic anhydride. The reaction is carried out at 600 atm and 230°C in the presence of iodide-promoted cobalt catalyst to form acetic acid at over 90% yield. In the presence of rhodium catalyst the reaction occurs at milder conditions at 30 to 60 atm and $150\text{--}200^\circ\text{C}$. Carbon monoxide can combine with higher alcohols, however, at a much slower reaction rate.

Carbonylation of acetic acid to higher carboxylic acids can occur in presence of ruthenium/iodide catalysts. The reaction involves reduction and several carbonylation steps. The overall reaction may be written as follows:

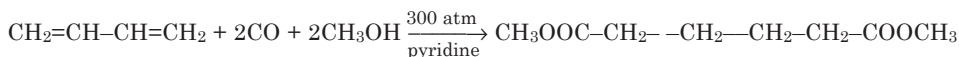


Carbonylation of olefins produces aldehydes that are converted to other deriv-

atives. Reaction with ethylene yields acrolein:

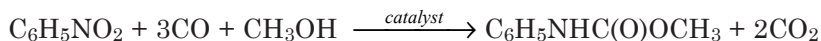


Carbonylation of butadiene at 300 atm, catalyzed by dicobalt octacarbonyl in presence of pyridine and subsequent methylation produces methyl ester of adipic acid. The overall reaction is as follows:

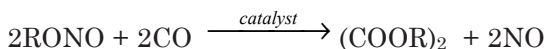


Hydrolysis of the ester forms adipic acid, used to manufacture nylon-6.

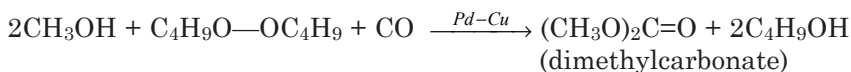
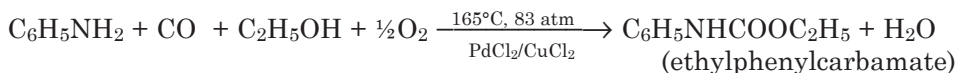
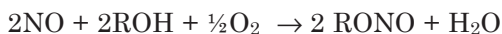
Carbonylations of nitroaromatics are used to synthesize an array of products including amines, carbamates, isocyanates, ureas and azo compounds. These reactions are catalyzed by iron, ruthenium, rhodium and palladium complexes. For example, carbonylation of nitrobenzene in the presence of methanol produces a carbamate:



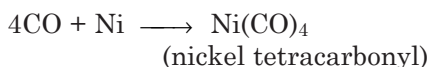
Oxidative carbonylation reactions have been employed successfully to produce a variety of industrial products. The reaction involves carbonylation in the presence of oxygen or oxidizing agents. These reactions occur at 150–200°C and 50 to 100 atm in the presence of palladium or other noble metal catalysts. Synthesis of oxalate ester to produce ethylene glycol, carbonylation of aniline to obtain alkylphenylcarbamate, and synthesis of dimethylcarbonate are some examples of such oxidative addition of carbon monoxide. The overall equations for these reactions are:

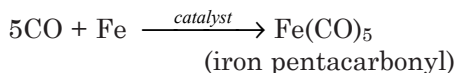


where R is an alkyl group; RONO is obtained by the reaction:



Carbon monoxide reacts with many finely divided metals under pressure, forming carbonyls:





In liquid ammonia, CO reacts with alkali metals forming white solid metal carbonyls.

Carbon monoxide thermally decomposes to carbon and CO₂ when heated from 500 to 700 °C; while catalytic decomposition occurs at ambient temperatures in presence of Pd/silica gel or MnO₂/CuO catalysts.

Analysis

Elemental composition: C 42.88%, O 57.12%. Carbon monoxide may be identified and determined quantitatively at low ppm level by infrared sensors. Such CO detectors are commercially available. Also, it can be analyzed by GC using TCD or FID or by GC/MS. The characteristic ion mass for CO identification is 28 (same as N₂ or ethylene, both of which can interfere).

Hazard

Carbon monoxide is a highly flammable and poisonous gas. Its flammable limits in air are 12.5 to 74.2% by volume, and the autoignition temperature 700°C. It explodes when exposed to flame. Reactions with interhalogen compounds, such as, bromine pentafluoride or halogen oxides can cause explosion. It forms explosive products with sodium or potassium that are sensitive to heat and shock.

Carbon monoxide binds to hemoglobin, the oxygen carrier in blood, forming carboxyhemoglobin. This prevents transport of oxygen through blood into all tissues in the body. The toxic symptoms are headache, dizziness, weakness, nausea, vomiting, loss of coordination, respiratory depression, decreased pulse rate, collapse, and unconsciousness. Brief exposure to high concentrations of this gas can cause death from asphyxiation. A 5 minute exposure to 5,000 ppm can be lethal to humans.

CARBON SUBOXIDE

[504–64–3]

Formula: C₃O₂; MW 68.032; Structure O=C=C=C=O

Synonyms: tricarbon dioxide; 1,2–propadiene–1,3–dione

Uses

Carbon suboxide is used in the preparation of malonates; and as an auxiliary to improve dye affinity of fibers.

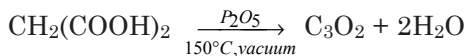
Physical Properties

Colorless gas; strong, pungent odor; gas density 2.985 g/L; liquid density 1.114 g/mL at 0°C; refractive index 1.4538 (at 0°C); vapor pressure 588 torr at 0°C; liquefies at 6.8°C; freezes at –111.3°C; burns with a blue sooty flame; reacts

with water. The compound is unstable, polymerizing on storage.

Preparation

Carbon suboxide is prepared by dehydration of malonic acid with phosphorus pentoxide in vacuum at 140 to 150°C:



Alternatively, the compound may be prepared by thermal dissociation of diacetyltartaric anhydride.

Reactions

Carbon suboxide decomposes slowly in water giving malonic acid:



Reaction with ammonia gives malonamide:



Similar reaction occurs with amines and imines; the decomposition is rapid:



Photolysis produces unstable dicarbon oxide, C_2O , which reacts with olefins (Cotton, F.A., G. Wilkinson, C.A. Murillo and M. Bochmann, 1999. In *Advanced Inorganic Chemistry*, 6th ed. p 226, NY: Wiley Interscience). C_3O_2 polymerizes slowly at ambient temperature forming yellow to violet products. The products are soluble in water.

Analysis

Elemental composition: C 52.96%, O 47.04%. It may be analyzed by treatment with water. The product malonic acid formed may be measured quantitatively by direct injection of aqueous solution into a GC for FID detection. Alternatively, the aqueous solution may be evaporated and the residue may be derivatized to methyl ester and identified by mass spectrometry. Also, the gas may react with ammonia or an amine, and the amide derivative may be identified and quantitatively determined by GC-FID, GC-NPD, GC/MS or infrared techniques.

Hazard

Carbon suboxide forms explosive mixtures in air. The lower and upper explosive limits are 6 to 30% by volume in air, respectively. The gas is a strong lacrimator and an irritant to eyes, nose and respiratory tract. Exposure to high concentrations is dangerous. .

CARBON TETRACHLORIDE

[56-23-5]

Formula: CCl_4 ; MW 153.82; tetrahedral structure; a nonpolar molecule with zero dipole moment.

Synonyms: tetrachloromethane; perchloromethane

Uses

Carbon tetrachloride is used in refrigerants; in fumigants for crops; in metal degreasing; and in the manufacture of semiconductors. It also is used as a solvent in many industrial processes. It is an excellent solvent for organic compounds that are nonpolar or have low polarity.

Physical Properties

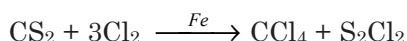
Colorless noncombustible liquid; chloroform-like odor; refractive index 1.4601; density 1.5867 g/mL at 20°C; boils at 76.8°C; freezes at -23°C; critical temperature 283.5°C, critical pressure 44.57 atm, critical volume 276 cm³/mol; practically insoluble in water; soluble in alcohol, ether, chloroform and benzene.

Thermochemical Properties

ΔH_f°	-32.37 kcal/mol
ΔG_f°	-15.60 kcal/mol
S°	51.72 cal/degree mol
C_p	31.49 cal/degree mol
ΔH_{fus}	0.78 kcal/mol

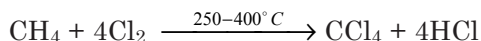
Production

Carbon tetrachloride is made by the reaction of carbon disulfide and chlorine in the presence of a catalyst, such as iron or antimony pentachloride:



Sulfur chloride is removed by treatment with caustic soda solution. The product is purified by distillation.

Alternatively, CCl₄ may be prepared by heating a mixture of chlorine and methane at 250 to 400°C.



Analysis

Elemental composition: C 7.81%, Cl 92.19%. Carbon tetrachloride may be analyzed by GC or GC/MS. For GC determination, an FID or a halogen-specific detector such as ECD or HECD may be used. Trace concentrations in aqueous matrix or soil, sediments or solid wastes may be determined by 'purge and trap' or thermal desorption techniques followed by GC or GC/MS measurements. The characteristic masses for identification of CCl₄ by GC/MS are 117, 119 and 121.

Different sampling techniques are documented for analysis of CCl₄ in the air (Patnaik, P. 1997. *Handbook of Environmental Analysis*. Boca Raton, FL: Lewis Publishers).

Toxicity

Carbon tetrachloride is a poison and also a carcinogen. The acute toxicity

of this compound in humans is of low order. However, the ingestion of the liquid can be fatal, death resulting from acute liver or kidney necrosis. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons.) The acute poisoning effects are headache, dizziness, fatigue, stupor, nausea, vomiting, diarrhea, and liver damage. Chronic exposure can damage both liver and kidney. Carbon tetrachloride also is a suspected human carcinogen. It causes liver and thyroid cancers in experimental animals.

CARBONYL CHLORIDE

[75–44–5]

Formula: COCl_2 ; MW 98.915

Synonyms: phosgene; carbon oxychloride; chloroformyl chloride; carbonic dichloride

Uses

Carbonyl chloride is used in the manufacture of isocyanates, polycarbonate resins, polyurethane, carbamate pesticides and herbicides and dyes. It was used as a war gas.

Physical Properties

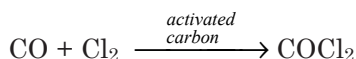
Colorless gas at ambient temperature; strong, pungent odor; density of the gas 4.045 g/L at 25°C; density of the liquid 1.392 g/mL at 4°C; liquefies to a light yellow fluid at 8.2°C; freezes at –128°C; critical temperature 182°C, critical pressure 55.96 atm, critical volume 190 cm³/mol; slightly soluble in water with slow hydrolysis; soluble in benzene, toluene and acetic acid.

Thermochemical Properties

ΔH_f°	–52.30 kcal/mol
ΔG_f°	–48.90 kcal/mol
S°	67.74 cal/degree mol
C_p	13.78 cal/degree mol
ΔH_{fus}	1.37 kcal/mol

Preparation

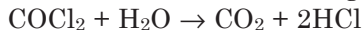
Phosgene is prepared by the reaction of carbon monoxide and chlorine. The mixture of these gases is passed over activated carbon:



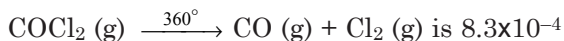
Alternatively, phosgene can be made by reacting carbon monoxide with nitrosyl chloride, or by treating carbon tetrachloride with oleum.

Reaction

Phosgene reacts with water forming hydrochloric acid and carbon dioxide:



When heated at elevated temperatures, it decomposes to carbon monoxide and chlorine. The equilibrium constant, K_c at 360°C for the reaction

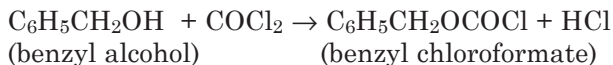
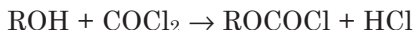


In a closed container at an initial concentration of 0.5 mol/L, the above K_c value corresponds to a 4% decomposition. However, if the concentration is decreased to 0.01 mol/L, the corresponding decomposition of phosgene to carbon monoxide and chlorine at 360°C is 25%.

Reaction with ammonia yields urea:



Reaction with alcohol can produce two different types of products. While two molar equivalent of alcohol yields dialkyl carbonate, with one molar equivalent of alcohol the product is an alkyl chloroformate:



Analysis

Elemental composition: C 12.14%, O 16.17%, Cl 71.69%. Phosgene can be analyzed by GC using FID or a halogen-specific detector; or by GC/MS. Ambient air may be collected in a metal container placed in an argon bath or condensed into any other type cryogenically cooled trap. Alternatively, the air may be collected in a Tedlar bag. The sampled air may be sucked by a condensation mechanism into the GC column.

Carbonyl chloride in air at maximum allowable concentration may be measured by colorimetry. Prepare a solution containing 5% *p*-dimethylaminobenzaldehyde and 5% diphenylamine in carbon tetrachloride. Soak a paper in this solution. Allow it to dry. The color of the paper turns from yellow to deep orange in the presence of carbonyl chloride.

Toxicity

The gas is treacherously toxic, as its effects cannot be recognized immediately. The initial symptoms are mild. Death can result from severe congestion of lungs or pneumonia several hours after exposure. Toxicity is due to HCl forming from its reaction with water. The symptoms are coughing, burning of the throat, choking, chest pain, vomiting, difficulty in breathing, and

cyanosis. Inhalation of this gas at 100 ppm concentration in the air for 30 minutes may be fatal to humans. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons.)

CARBONYL FLUORIDE

[353–50–4]

Formula: COF₂; MW 66.01

Synonyms: carbon oxyfluoride; carbonyl difluoride; fluoroformyl fluoride; fluorophosgene

Uses

No commercial application of this compound is known.

Physical Properties

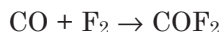
Colorless gas; pungent odor; hygroscopic; unstable; liquid density 1.139 g/mL (at –114°C); liquefies at –83.1°C; solidifies at –114°C; decomposes in water.

Thermochemical Properties

ΔH_f°	–151.7 kcal/mol
ΔG_f°	–148.0 kcal/mol
S°	61.78 cal/degree mol
C_p	11.19 cal/degree mol

Preparation

Carbonyl fluoride is prepared by the reaction of carbon monoxide with fluorine gas or silver fluoride:



Also, it may be produced by the action of carbon monoxide with bromine trifluoride, BrF₃.

Analysis

Elemental composition: C 18.19%, F 57.57%, O 24.24%. Carbonyl fluoride may be analyzed by FTIR, GC or GC/MS. For the GC analysis, it may be transported with the carrier gas helium from the reaction vessel into a cryogenically cooled injector port, then thermally desorbed and analysed by FID. The system should be free of moisture. The characteristic ions for mass spectroscopic identification are 66, 26, and 40.

Toxicity

Carbonyl fluoride is a strong irritant to the eyes, nose and respiratory tract. Contact with skin can cause irritation. Prolonged exposure to high concentrations of this gas is lethal.